

# PATENT SPECIFICATION

NO DRAWINGS

1.156.954



1.156.954

Date of Application and filing Complete Specification: 22 June, 1967.

No. 28845/67.

Application made in United States of America (No. 559750) on 23 June, 1966.

Complete Specification Published: 2 July, 1969.

© Crown Copyright 1969.

Index at acceptance:—C3 R(32D1, 32D4, 32E3, 32G2, 32J3)

Int. Cl.:—C 08 g 22/06

## COMPLETE SPECIFICATION

### Improvements relating to Polyurethanes

- We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 61 Broadway, New York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- THIS INVENTION relates to curable polyurethane compositions having an extended pot life. More particularly, it relates to polyurethane prepolymer compositions containing a chain extender which remain pourable and workable for prolonged periods, and to the preparation thereof.
- Polyurethane elastomers can be cast or moulded in many intricate shapes and forms to produce for example solid tyres, anti-vibration mountings, impellers, propellers, bushings, bearings, chute linings, gears, belts, protective equipment, helmet liners, and gas masks. The general method of preparing polyurethane elastomers involves the preliminary formation of a prepolymer by co-reacting a polyol, e.g. a polyester having terminal hydroxyl groups or a polyether glycol, with stoichiometric excess of polyisocyanate. The resultant isocyanate terminated prepolymer is cured by reaction with a polyfunctional cross-linking or chain extending agent containing active hydrogen, such as water, an aromatic or aliphatic diamine, or an aliphatic diol; such an agent will hereinafter be referred to as a "curing agent". Non-reactive ingredients such as fillers, dyes, and anti-oxidants may be added, as desired, at this stage.
- The curing step is carried out by first admixing, and preferably thoroughly blending, the prepolymer with the curing agent, usually at elevated temperature. The mixture is then poured into moulds and hardened by the application of heat and/or pressure, or it is masticated on heated rolls and formed into sheets.
- In most instances, the mixture of prepolymer and curing agent remains in a fluid pourable condition for a relatively short time. Such compositions are said to have a relatively short "pot life". This necessitates the preparation of such mixtures in small batches. This is inconvenient and expensive, and not conducive to large scale manufacture. Moreover, the short pot life of these curable compositions often makes the filling of the moulds, especially those of intricate shape, difficult and incomplete, and entrapment of gas bubbles often occurs. When the curable compositions are maintained above 25°C for long periods, as often occurs since temperatures above 25°C are generally necessary for the satisfactory preparation of both prepolymer and cured elastomer, they will often not remain even sufficiently fluid to be poured into moulds which adds to the difficulties of economic production of the moulded articles.
- The present invention is concerned with curable polyurethane compositions having extended pot life, which remain sufficiently fluid to be poured into moulds even when maintained at above 25°C for extended periods. The compositions of the invention comprise an intimate mixture of an isocyanate-terminated prepolymer which is the reaction product of a polyester polyol and methylene bis(4-cyclohexylisocyanate), and an arylene diamine as curing agent. They can be maintained at temperatures above 25°C for substantially longer periods without losing their fluid character than curable compositions derived from polyurethane prepolymers prepared from more conventional polyisocyanates such as tolylene diisocyanates.
- The curable polyurethane compositions of this invention can be prepared in the conventional manner. In a preferred method a

[Price 4s. 6d.]

polyester polyol, formed from ethylene glycol, propylene glycol and adipic acid, is reacted with methylene bis(4-cyclohexylisocyanate).

- 5 The resultant isocyanate rich prepolymer is mixed with sufficient of the curing agent, e.g. 4,4' - methylene - bis - (2 - chloroaniline), to react with 80—100% of the free isocyanate groups. The mixture is vigorously agitated and then poured into a pre-heated mould.
- 10 The pot life of the mixture can be determined by inserting a wooden tongue depressor into the hot mixture and removing the depressor. When the cavity made by the depressor does not disappear, the mixture is no longer pourable and the pot life is said
- 15 have ended. The mixture when poured into the pre-heated mould can be cured in any known manner, for example, it can be heated at 135°C under 2,800 kg/cm<sup>2</sup> pressure for 10
- 20 minutes and post-cured for 3 hours at 130°C.

- The resultant elastomers after curing in a conventional manner have all the usual excellent physical properties of polyurethane elastomers such as high tensile strength, hardness, resistance to solvents, and abrasion resistance.
- 25 A stoichiometric excess of isocyanate over polyol is used to prepare the prepolymers. Preferably this excess should be such as to provide at least 3.0% and especially from
- 30 5 to 7% by weight of free isocyanate groups in the prepolymer.

- The polyester polyol (which term includes polyesteramide polyols) used to prepare the prepolymer is preferably a linear compound having terminal hydroxyl groups and a functionality of 2. Such compounds are well known in this art and may be prepared in a conventional manner by condensation of one
- 35 or a mixture of dibasic acids and one or a mixture of glycols. Representative examples of the dibasic acids which can be used in the preparation of these polyesters are succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, and terephthalic acids. Suitable glycols include ethylene glycol, propylene glycol, butylene glycol, tetramethylene glycol and hexamethylene glycol. Polyester polyols derived from adipic acid and a mixture
- 40 of ethylene and propylene glycols are preferred. The polyester polyols desirably have a molecular weight of at least 1000, preferably between about 1500 and about 2500. Their hydroxyl number should be between 40 and 115 and the acid number below 5.
- 45 In the formation of the polyurethane elastomer the prepolymer containing free isocyanate groups is caused to react with the
- 50 arylene diamine curing agent. Examples of arylene diamines which may be used are 4,4' - methylene - bis - (2 - chloroaniline), 4,4' - methylene - bis - (2 - bromoaniline), 4,4' - methylene - bis - (2 - methoxyaniline), 4,4' -
- 55 methylene - bis - (2 - ethylaniline), 4,4' -

methylene - bis - (2 - n - hexylaniline, naphthalene - 1,5 - diamine, 2,2'-dichlorobenzidine, and dianisidine.

The amount of the curing agent used is generally between 80% and 100%, e.g. 90%, of the amount theoretically required to react with all the free isocyanate groups in the prepolymer.

The following Examples illustrate the invention. All parts and percentages are by weight unless otherwise specified and temperatures are in °C.

#### EXAMPLE 1

##### Control Experiment

A polyester having an average molecular weight of about 2100, a hydroxyl number of about 57 and an acid number below 3, was prepared by polycondensing adipic acid with a mixture of glycols containing 80 mol % of ethylene glycol and 20 mol % of propylene glycol. 100 parts of this polyester were heated to 45°—50°, and 27.5 parts of a mixture of 80% 2,4- and 20% 2,6-tolylene diisocyanate were added. The mixture was heated to and maintained at 80° for 3 hours. The resultant prepolymer containing 6.84% unreacted NCO groups.

100 parts of the prepolymer were heated to 110° and there were then added 19.55 parts of 4,4' - methylene - bis - (2 - chloroaniline), representing 90% of the theoretical amount required to react with all the free NCO groups of the prepolymer. The mixture was agitated vigorously for 15 to 25 seconds, and poured into a mould pre-heated to 130°. The pot life of the mixture as determined by the wood tongue test referred to above was 47 seconds.

#### EXAMPLE 2

A mixture of 200 parts of the ethylene/propylene adipate polyester described in Example 1 above heated to 45—50° and 83 parts of methylene - bis - (4 - cyclohexylisocyanate) was heated to and maintained at 78° to 80° for 3 hours. The mixture was permitted to cool by standing at ambient temperature for about 16 hours. The prepolymer contained 6.07% free NCO groups.

70 parts of this prepolymer were heated to 110° and to it were added 12.1 parts of 4,4' - methylene - bis - (2 - chloroaniline) which also was heated to 110°. The mixture was agitated vigorously for about 30 seconds and then poured into a mould, pre-heated to 130°. The pot life of this curable mixture as determined by the wood tongue test was 20 minutes.

It can thus be seen that polyurethane compositions having a very long pot life can be obtained.

#### WHAT WE CLAIM IS:—

1. A curable polyurethane-forming composition having an extended pot life com-

- prising an intimately blended mixture of an isocyanate-terminated polyurethane prepolymer which is the reaction product of a polyester polyol and methylene - bis(4 - cyclohexylisocyanate), and an arylene diamine as curing agent.
2. A composition according to Claim 1, wherein an amount of curing agent sufficient to react with 80% to 100% of the free isocyanate groups present in the prepolymer is used.
3. A composition according to Claim 1 or 2, wherein the polyester polyol is a reaction product of ethylene glycol, propylene glycol and adipic acid.
4. A composition according to Claim 3, wherein the polyurethane prepolymer is the reaction product of poly(ethylene/propylene) adipate having an average molecular weight of between 1500 and 2500, and a hydroxyl number of between 40 and 115 and a stoichiometric excess of methylene - bis - (4 - cycloisocyanate).
5. A composition according to any preceding Claim, wherein the arylene diamine is 4,4' - methylene - bis - (2 - chloroaniline).
6. A composition according to Claim 1, substantially as herein described.
7. A composition according to Claim 1, as described in Example 2 herein.
8. A method of making a curable polyurethane-forming composition claimed in any preceding Claim, which comprises reacting the polyester polyol with a stoichiometric excess of methylene - bis - (4 - cyclohexylisocyanate) to form the isocyanate-terminated polyurethane prepolymer and thereafter intimately blending the prepolymer with sufficient of the curing agent to react with 80% to 100% of the isocyanate groups.
9. A method according to Claim 8, wherein the curing agent and prepolymer are separately pre-heated prior to intimate blending.
10. A method according to Claim 8, substantially as herein described.
11. Curable polyurethane compositions when obtained by a process claimed in any one of Claims 8—10.
12. Moulded or shaped articles made of polyurethane elastomers produced by curing a composition claimed in any one of Claims 1 to 7 and 11.

J. A. KEMP & CO.,  
Chartered Patent Agents,  
14 South Square,  
Gray's Inn, London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.

Published by the Patent Office, 25, Southampton Buildings, London, W.C.2. from which copies may be obtained.